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Microstructures, stress, strain and surface characterization of TD polycrystalline CdS thin films

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Abstract : We report in this paper the effects of substrate temperature (Ts) and film thickness (T_f) on the microstructures, stress, strain and the surface morphology in thermally deposited (TD) polycrystalline CdS thin films using XRD and SEM techniques The XRD and the SEM results reveal that the quality of polycrystalline nature of CdS films grown under identical film growth conditions were observed significantly improved with Ts and T_f The structural phases of the films were observed to possess two phase structures Films grown at Ts $\leq$ 423K were found f c c. cubic ZnS structure with (111), (220) and (311) planes, and hexagonal phase structure at Ts $\geq$ 443K with (002) and (112) planes The evaluated lattice parameters in cubic and hexagonal phases were found with close agreements with their standard values. The films were observed to contain a large regions of localized micro-strains, the sizes of which were observed to decrease as Ts increases from 373K to 473K in films of 2500Å thickness, and T_f increases from 1500Å to 4000 Å at 473K (Ts) The films grown from 300K to 423K (Ts) were found to be unstressed, and fairly stressed at elevated Ts The stresses were remarkably increased with increasing T_f

Keywords · CdS thin films, XRD, SEM, substrate temperature, film thickness, stress, strain

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1. Introduction

The physical properties of a thin solid film are characterized by its structure sensitive properties like crystalinity, structural phase, lattice constants, grain-size *etc.* which influence remarkably on the mechanical, optical and photo-electronic properties of the film. Attention is, therefore, given to structural analysis of the films, particularly the CdS thin fims by different deposition techniques [1-8] correlating electrical, optical and photo-electronic properties of the films. A vacuum evaporated thin film may be either amorphous or polycrystalline in nature. A polycrystalline thin film generally contains a large number of

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crystallites of various sizes oriented quite haphazardly. These are known as grains, the sizes of which are closely related to the transport properties of the films. The grain-sizes increase with Ts, particularly beyond the re-crystallization temperature of the film and T_f XRD technique was used for structural analysis. It was observed that CdS thin films possess f.c.c. cubic zinc blend structure below Ts ≤ 423K with most preferential orientation along (111) plane at 2θ = 26.45^0. The values of $\sin^2\theta_1/\sin^2\theta_2$ corresponding to (111) and (220) planes could confirm the f.c.c. cubic structure of the film with orientation along (111) plane parallel to the substrate, while hexagonal ZnS (wurtzite) structure was obtained at Ts ≥ 443K with strong reflection plane along (002) at 2θ = 26.450 parallel to the substrate and c axis perpendicular to the substrate as confirmed by JCPDS – X-ray powder file data [9,10]. A two phase structures sphelerite and wurtzite structures were, therefore, expected between 423K and 443K. Similar results were also obtained by other workers [11-14]. The lattice parameters in both cubic and hexagonal structures were evaluated, and the systematic errors in measurements of 2θ in XRD data corresponding to each plane of reflections in the films, were eliminated from Nelson – Riley (N-R) plots The internal stress and micro-strains in the films developed owing to the effects of *Ts* and T_f were also systematically evaluated.

2. Experimental details

CdS bulk powder (Koch Light Laboratory, UK with purity 99.999%) was used as the source material for the present work. The material has density of 4.8 x 10^3 Kg m^{-3} and m.p.~ 1750^{0}C under normal atmospheric pressure. Some amount of sample was taken Prior to the deposition of the films, the material was dried and then grinded into fine powder form. Tantalum (Ta) boat (m.p. ~ 2990^{0}C and density ~ 16.6 x 10^3 Kgm^{-3}) was prepared from Ta –sheet (M/S Hind High Vacuum Co. Pvt. Ltd., Bangalore) and was used as the heater for deposition of the sample. CdS thin films of thickness 2500Å at different Ts in the range (300 – 473)K, and T_f in the range (15 – 40) x *n* where *n* =100Å at Ts = 473K were suitably deposited on chemically and ultrasonically cleaned glass substrates by means of HINDHIVAC (12A4) coating unit. The substrate temperatures of the films were measured with the help of a copper – constantant thermocouple coupled with a digital micro-voltmeter, and the thickness of the films were measured with the help of a suitably designed Multiple Beam Interferometer with an accuracy of ± 15Å. The vacuum maintained was ~ 1.33 x 10^{-4} Pa. The rate of deposition of the films was controlled properly by controlling the heater current, and was maintained between (2.14 – 2.50) ÅS^{-1}. The as grown CdS thin films had a dimension of 10 x 10 x 1.35 mm^3. The structural characterizations of the films were determined by means of Phillips X' pert Pro – Automated Powder X-ray (model APD 1700) diffractometer with CuK_α – radiations (λ = 1.572A). The X-ray tube was operated at 40KV – 20mA for all the present observations. The surface morphology of the films was studied with the help of JEOL JSM – 6360 Scanning Electron Microscope (SEM) computerized with EIZO FLEXSCAN T566. For SEM studies appropriate film sizes 7.0 x 7.0mm^2 were suitably cut with the help of a fine diamond head cutter.

3. Results and discussions

3.1. Effect of substrate temperature on structural properties

The XRD patterns of CdS thin films of T_f 2500Å grown at *Ts*, 300K, 423K and 473K are shown in Figures 1(a, b and c), which reveal the polycrystalline growth of the films The diffraction patterns clearly reveal peaks corresponding to cubic f.c.c. zinc blend structure at 2θ = 26.50°C at *Ts* in the range (373 – 423)K with most preferential reflections along

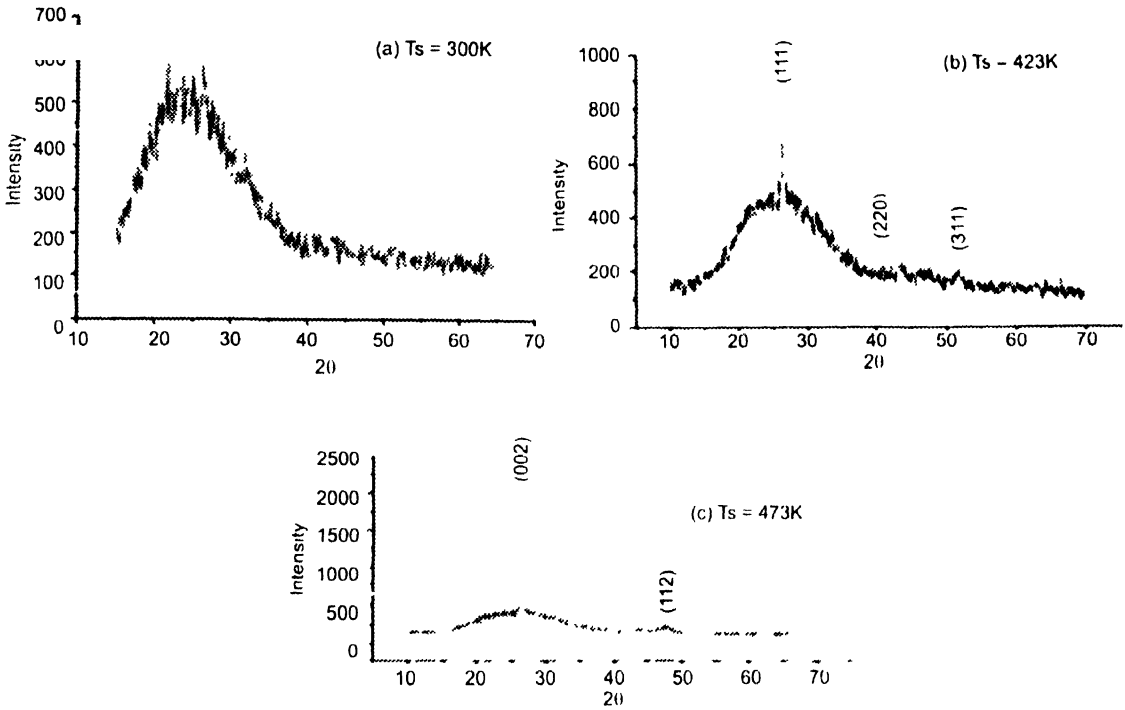

Figure 1. (a, b and c) XRD patterns of CdS thin films, 2500Å at different Ts

(111) plane together with some other small peaks at (220) and (311) planes. The films grown at elevated Ts (473K) show sharp peak at 2θ = 26.45° with most preferential reflection along (002) plane with other reflection (112) plane, which shows the hexagonal wurtzite structure [9,10]. It is observed that the peak heights increase with increasing Ts. The lattice parameters in cubic phase were evaluated using the relations

$$a_{cal} = \lambda\sqrt{\left(h^2 + k^2 + l^2\right)}/2\sin\theta \tag{1}$$

$$d_{cal} = a_{cal}/\sqrt{\left(h^2 + k^2 + l^2\right)} \tag{2}$$

and in hexagonal phase, using Vegerd's law

$$a_{hex} = \sqrt{1/2}a_{cal}, \text{ and } c_{cal} = \sqrt{4/3}a_{cal} \tag{3}$$

$$1/d^2 = 4/3\left[h^2 + hk + k^2\right]/a^2 + l^2/c^2 \,. \tag{4}$$

The systematic errors in measurements of 2θ corresponding to each plane of reflections were eliminated with the help of N-R plots.

3.2. Effect of substrate temperature on grain-sizes, average stress and strains :

The grown CdS thin films consist of various grains of different sizes oriented haphazardly, which depend on *Ts*. The grain or crystallite sizes were calculated using the Scherrer formula [16]

$$D_{hkl} = k\lambda/\beta_{2\theta}\cos\theta \tag{5}$$

where the value of shape factor k is taken as 0.94, $\beta_{2\theta}$, the width of the peak at half of the maximum peak intensity and θ the Bragg angle.

Figure 2 shows the variation of grain – size with Ts of the films. It is observed that grain-sizes increase with increasing Ts from 180Å (Ts = 373K) to 229Å (Ts = 423K) beyond which it increases rapidly to 305Å (*Ts* = 473K) as also been observed in the SEM micrographs from Figure 3(a and b).

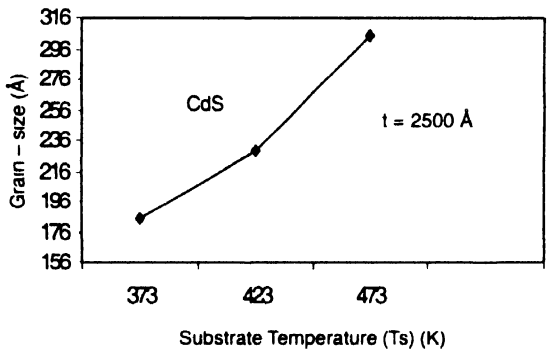

Figure 2. Grain Size *vs.* Ts plot.

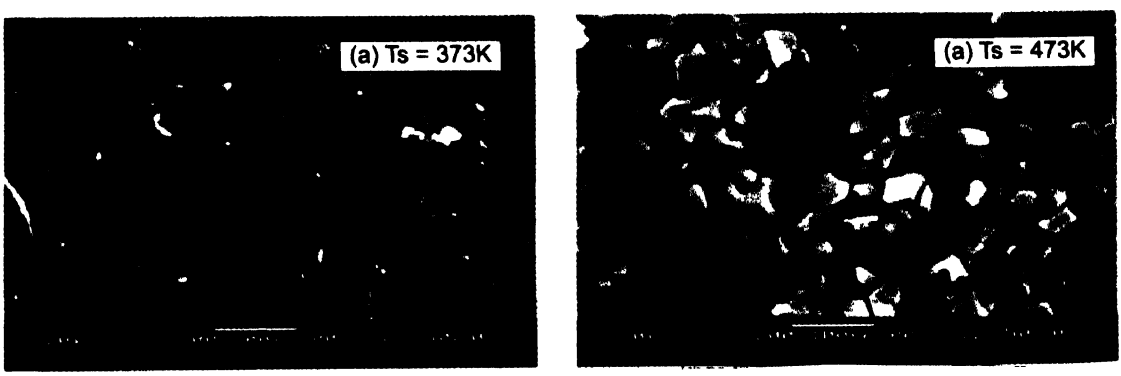

Figure 3 (a and b). SEM micrographs of CdS films, 2500Å (t) at different Ts.

The films were observed under various stresses on account of some thermal expansion co-efficient of the films and the substrates at different Ts, which depended on various factors like lattice parameters, grain-sizes, orientation of grains [17,18]. The stresses were calculated using the relation[19,20]

$$S = E/2\gamma\,(a_0 - a)/a_0 \tag{6}$$

where a_0 and a are the lattice parameters of CdS bulk and thin film materials, E and γ the Young's modulus and Poisson's ratio of the material of the films respectively Standard values of a_0 [21], E and γ [22] for CdS bulk material were used for calculation of stress The peak width $\beta_{2\theta}$ used to obtain the grain – size can be assumed to be an exclusive contribution for obtaining micro-strains. The micro-strains were calculated using the relation [23]

$$\varepsilon = \beta_{2\theta}\,[Cot\,\theta/4]\,. \tag{7}$$

Table 1. d_{hkl}- values at different Ts of the CdS thin films

hkl	JCPDS	I/I0	f.c.c cub ZnS structure at Ts						h.c.p structure	
	d(Å)		300K		373K		423K		at Ts = 473K	
			2θ	d (Å)	2θ	d (Å)	2θ	d (Å)	2θ	d (Å)
111	3.362	100		.	26 455	3 366	26 50	3 361		
220	2.069	43	..	.			43 85	2 066		
311	1.756	30	....	. .	52 450	1 746	52 00	1 760		
002	3.367	100	.		..	. .			26 45	3 894
112	1.761	60	..						47 53	1 789

Table 2. Lattice parameters, micro-strains and av stress in CdS films at different Ts

Ts (K)	hkl (Å)	JCPDS- standard (Å)	a_{cal} (Å)	a_o from NR-plots	micro-strains ι (x 10^4)	av stress (GPa)
	111		5 830	5 83	83.51	
373	200	5.83	5.537			
	311		5 790			
	111		5.830	5 83	65 71	
423	220	5.83	5.843			
	311		5 837			

			h.c.p. –structure						
			a_{cub}	a_{hex}.a_o from N-R plot		c_{hex}.	d_{hex}	ε (x 10^{-4})	av.Stress
			(Å)	(Å)	(Å)	(Å)	(Å)		(GPa)
	002		6.745	4 769		7.787	3.394	48.94	
473	112	a = 4.136 Å	4.689	3.316	4.172	5.414	1 789		0.45
		c = 6.713 Å							

Table 3. d-values from XRD data of the films at different T_f grown at 473K (Ts).

hkl	JCPDS	1500Å		3500Å		4000Å	
		$2\theta^0$	d (Å)	$2\theta^0$	d (Å)	$2\theta^0$	d (Å)
002	3.367	26.55	3.864	26.50	3.887	28.50	3.887
103	1.898			48.10	1.951	48.55	2.284
112	1.761			52.30	1.293	52.30	1.293

Table 4. Lattice parameters, micro-strains and av. stress in T_f dependent CdS films.

T_f (Å)	hkl	JCPDS	a_{hex} (Å)	c_{hex} (Å)	a_0 from N-R plot (Å)	micro-strain ϵ (x 10^{-4})	av. stress (GPa)
1500	002		4.7515	7.728	....	52.0	....
	002	a = 4.136	4.760	7.773			
3500	103	c = 6.713	4.233	6.911	4.190	44.91	0.71
	112		3.618	4.951			
4000	002		4.760	7.773			
	103		4.326	6.852	4.235	38 38	1 292
	112		3.032	4.951			

Table 5. Values of grain-sizes measured at different Ts and T_f of the films

Values	Ts (K), T_f = 2500Å				T_f (Å), (Ts = 473K)			
	300	373	423	473	1500	2500	3500	4000
$\beta_{1/2}$ (degree) →	....	0.45	0.355	0.264	0.282	0.243	0.242	0.207
2θ (degree) →	.....	26.46	26.50	26 45	26.50	26.49	26.50	26.49
D_{hkl} (Å) →	.....	180	229	305	287.2	333.64	333.56	390

where $\beta_{2\theta}$ and θ were evaluated from the corresponding XRD spectra. The crystal has 4 atoms per unit cell with unit cell dimension a = 5.83Å, 5.843Å and 5.837Å corresponding to (111), (220) and (311) planes respectively supporting the f.c.c. cubic zinc sulphide structure. Further, the $\sin^2\theta_1/\sin^2\theta_2$ value corresponding to the first two reflection planes (111) and (220) which yielded 0.75 confirmed the cubic structure [24] with reflection along (111) plane parallel to the substrate, while the crystal exhibits hexagonal wurtzite structure at Ts ≥ 443K with strong orientation along (002) plane parallel to the substrate and c axis perpendicular to the substrate [9,10]. A two phase structures-spheralite and wurtzite are expected to exist between Ts, 423K – 443K. Similar results were also reported by other workers [11,12,13,14]. Table 1-shows a comparative study of observed d-values with JCPDS standard values in both structural phases in the reflection planes, and were in close

agreements with standard values. The lattice parameters a_{cal}-values and a_0 from N-R plots as shown in Figures 4 (a and b) in the films are shown in Table 2.

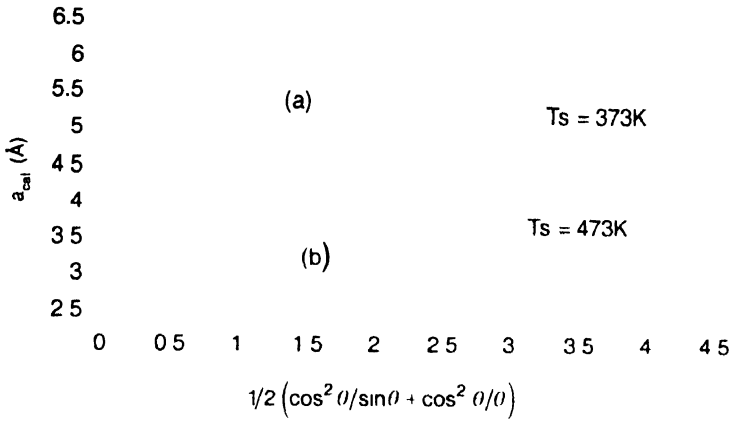

Figure 4 (a and b). Nelson-Riley plots of the films at different Ts

3.3. Effect of film thickness on micro-structural properties

Figures 5 (a and b) depict the XRD patterns of the films grown at 473K (Ts) with T_f 35n and 40*n* (with *n* assigned value as above) respectively. The diffraction patterns reveal the polycrystalline h.c.p. (wurtzite) structure with preferential reflections along (002), (103) and (112) planes which was improved with increasing T_f.

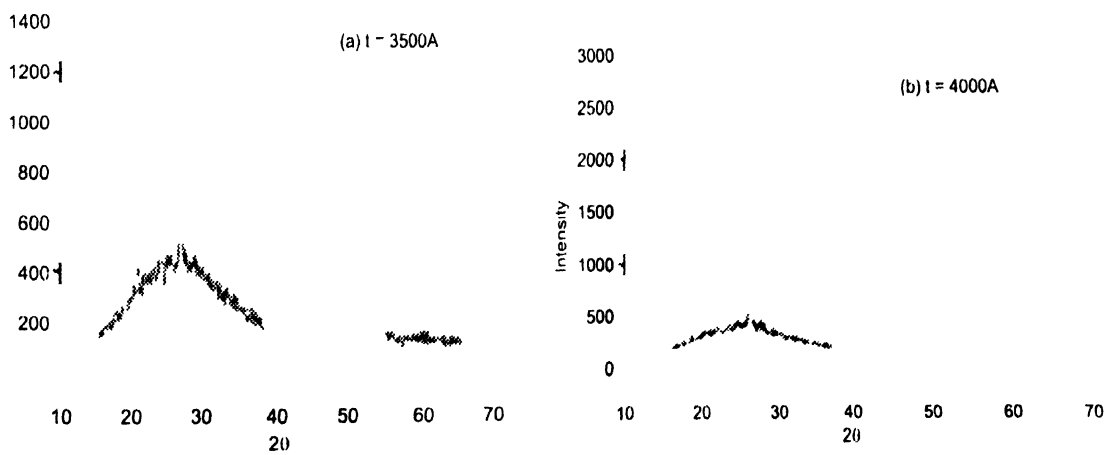

Figure 5 (a and b). XRD patterns of CdS films at different thickness

The lattice parameters evaluated with the help of eqs. (1), (2), (3) and (4) along with micro-strains and average stress in the films have been shown in Tables (3 and 4). The values of a_0 determined from N-R plots of the films of T_f 35*n* and 40*n* (Figure not shown) as shown in Table 4, were observed in close agreement with their standard values. Table-5 represents the values of grain-sizes at different Ts at (111) plane and T_f at (002) plane of the films, and the variation with T_f at Ts at 473K has been shown in Figure 6.